

High-Precision Lead Isotope Ratio Measurement by Inductively Coupled Plasma Multiple Collector Mass Spectrometry

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An inductively coupled plasma (ICP) ion source coupled to a magnetic sector mass analyser equipped with seven Faraday detectors has been used to measure the lead isotope ratios in solutions of Sanshiro Pond sediment collected at the University of Tokyo, airborne particulates collected at Shinjuku in Tokyo and Merck multielement standard product number 97279494. A thallium correction technique was utilised to allow a simultaneous correction for mass bias. This work followed an earlier interlaboratory comparison study of the above-mentioned solutions using ICP quadrupole mass spectrometry, and has demonstrated a considerable improvement in analytical precision. The following isotope ratio measurements were recorded. Pond sediment solution containing 82 ng ml⁻¹ lead: $^{206}\text{Pb}/^{204}\text{Pb}=17.762\pm 0.014$; $^{206}\text{Pb}/^{207}\text{Pb}=1.1424\pm 0.0009$; $^{208}\text{Pb}/^{204}\text{Pb}=37.678\pm 0.034$. Airborne particulate solution containing 45 ng ml⁻¹ lead: $^{206}\text{Pb}/^{204}\text{Pb}=17.969\pm 0.006$; $^{206}\text{Pb}/^{207}\text{Pb}=1.1528\pm 0.0003$; $^{208}\text{Pb}/^{204}\text{Pb}=37.915\pm 0.021$. Merck multielement standard solution containing 100 ng ml⁻¹ lead: $^{206}\text{Pb}/^{204}\text{Pb}=19.255\pm 0.015$; $^{206}\text{Pb}/^{207}\text{Pb}=1.2238\pm 0.0004$; $^{208}\text{Pb}/^{204}\text{Pb}=38.476\pm 0.021$ (All errors are given as ± 2 standard deviations).

Keywords Inductively coupled plasma mass spectrometry, magnetic sector mass spectrometry, lead isotope ratio measurement, thallium based mass bias correction

Thermal ionisation mass spectrometry (TIMS) is a well-established method for measuring both radiogenic and non-radiogenic isotope ratios. The isotope ratio measurements of elements such as uranium, lead, neodymium and strontium are routinely accomplished to high levels of precision and accuracy. However, because the efficiency of thermal ionisation decreases as the ionisation potential increases, certain elements cannot be analysed by this technique. Thus, potential analytical areas remain unchallenged. Further disadvantages of thermal ionisation include the extensive sample preparation required to purify samples and the long analysis time required to generate acceptable data.

An inductively coupled plasma (ICP) is a convenient technique for the ionisation of sample materials. Used in conjunction with a quadrupole mass spectrometer (ICP-MS), it has become an essential tool for determining the elemental composition of sample solutions. Since a plasma source can ionise over 90% of the elements in the periodic table, the detection of most elements is theoretically possible. The sample preparation and analysis time are relatively short, since samples are introduced directly into the plasma from solution. However, plasma systems equipped with quadrupole mass analysers cannot achieve the isotope ratio precision and accuracy demonstrated by TIMS. Analysis is

limited by signal instability and the necessary sequential measurement of isotopic components. In addition, the Gaussian peak shape which is typical of a quadrupole analyser makes signal quantification more difficult than the "flat topped" peak shapes exhibited by magnetic sector TIMS.

The determination of lead isotope ratios is of major importance in geological, environmental and clinical studies. A description of TIMS applied to measuring lead isotope ratios has been detailed by Chow *et al.*¹ and Facchetti *et al.*² High-precision, thermal-ionisation, isotope-ratio measurements of lead have been used as a sensitive geo-chronometer.³ Less precise ICP quadrupole measurements have been used to ascribe the origin of gasoline pollution⁴ and to determine the concentration of the lead content in human blood.^{5,6} A review of the methods and applications of plasma source mass spectrometry for measuring isotope ratios has been discussed by Jarvis *et al.*⁷ Due to the convenience and analytical speed of plasma source mass spectrometers, they are likely to play an increasing part in such analysis over the coming years. In recognition of this, Furuta⁸ devised an interlaboratory comparison study designed to assess how precisely results in the literature could be compared. Three lead samples identified as pond sediment, airborne particulates and Merck multielement standard were distributed to seven laboratories throughout the world. A solution of the National Institute of

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Standards and Technology (NIST) Standard Reference Material (SRM) Pb981 was also supplied. A comparison of the measured lead isotope ratios with the NIST certified values allowed a measurement and, hence, a correction for any mass bias. Measurements of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratios were made. The results revealed significant measurement differences between laboratories. For example, the $^{206}\text{Pb}/^{204}\text{Pb}$ Merck multielement measurement varied between 17.231 and 19.741 while the $^{208}\text{Pb}/^{204}\text{Pb}$ measurement varied between 33.366 and 39.464.

A recent publication by Walder and Freedman⁹ described a novel ICP based mass spectrometry system designed for measuring isotopic ratios (Fisons Instruments Plasma 54 mass spectrometer). The instrument comprises a plasma source, an electromagnet and a detection system equipped with seven Faraday detectors. The sample solution is ionised within the plasma in the conventional way. These ions are accelerated through an electromagnet which simultaneously separates the isotopes by mass and focuses each isotope into one of the detectors. The isotope-ratio measurement is performed simultaneously, thus removing any signal variations as a limitation upon the measurement precision. Operation of the electromagnet is optimised so as to produce "top hat" peak shapes, which make an accurate quantification of the peak heights possible.

A subsequent publication by Walder *et al.*¹⁰ describes the measurement of isotope ratios with the Plasma 54 in more detail. Measurements of lead, neodymium and hafnium reference materials were presented. The measurement of neodymium and hafnium isotope ratios utilised their stable isotopic components to measure and, hence, correct for any mass bias. A measurement precision of less than 0.005% was obtained, thereby challenging the performance of TIMS. Since lead does not contain a stable isotopic pair, such an internal correction procedure was not possible. However, the paper described how lead reference materials were deliberately doped with thallium and simultaneous measurements of ^{203}Tl , ^{204}Pb , ^{205}Tl , ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes were made. A comparison of the measured $^{205}\text{Tl}/^{203}\text{Tl}$ ratio with the true ratio allowed a calculation of the mass bias. This mass-bias figure was then applied to simultaneously correct the measured lead ratios. This correction technique, first investigated by Longerich *et al.*¹¹ and Ketterer *et al.*¹², allowed accurate measurements of lead SRMs 981, 982 and 983 and removed the need for a separate calibration analysis.

It is an objective of this study to measure the lead isotope ratios of the interlaboratory reference materials utilising the thallium correction technique with the Plasma 54 system. The unique configuration of the Plasma 54 instrument should allow measurements of superior precision to those determined by quadrupole analysers. Measurements obtained by both techniques will be compared and discussed. This work will complement the original study by providing an additional data set for comparison and evaluation.

Experimental

Sample preparation

Three samples were chosen for analysis: 1) pond sediment collected at "Sanshiro Pond" at the University of Tokyo; 2) airborne particulates collected at Shinjuku in Tokyo; and 3) a 23 element standard solution prepared by Merck in the USA (Product No. 97279494). Sample preparation has previously been described.⁸ Briefly, this involved separately digesting 1 g of the pond sediment and airborne particulates in 11 ml of nitric acid and 8 ml of perchloric acid; 4 ml of hydrofluoric acid was added to remove any silica. The mixture was evaporated to dryness and 4 ml of nitric acid was added. The final weights of these stock solutions were adjusted to 100 g with distilled water. The following prepared solutions were supplied by Furuta for analysis with the Plasma 54 mass spectrometer: pond sediment containing 82 ng ml^{-1} lead; airborne particulates containing 450 ng ml^{-1} lead; Merck multielement standard containing 100 ng ml^{-1} lead and NIST Pb981 containing 100 ng ml^{-1} lead. The NIST Pb981 solution was subsequently diluted to 50 ng ml^{-1} using $18\text{ M}\Omega\text{ cm}^{-1}$ de-ionised water so that the sample of known isotopic composition was the least concentrated (Analysis of the airborne particulate solution in this study resulted in an ion current that saturated the Faraday amplifiers. The solution was therefore diluted to 45 ng ml^{-1}). The NIST, airborne particulates and pond sediment solutions were subsequently doped with thallium (Johnson Matthey, Specpure ICP-direct current plasma (DCP) standard) to a concentration exceeding that of the lead. Since the Merck multielement standard contained 100 ng ml^{-1} thallium as one of its 23 constituent elements, this was not doped.

Analytical procedure

To maximise sample transmission through the mass spectrometer, a high-efficiency nebulisation system was utilised (Fisons Instruments Mistral Nebulisation System).^{13,14} The sample solution was converted to an aerosol with a conventional Meinhard pneumatic nebuliser. The aerosol was then passed through the Mistral desolvation unit. This apparatus removed water vapour from the aerosol stream by a sequential heating and cooling cycle. This ensured that the bulk of the aerosol arriving at the plasma consisted of a solute, and not the solvent. The entrance to the mass spectrometer comprised the conventional arrangement of sample and skimmer cones.⁹ The operation of the Plasma 54 mass spectrometry system coupled with the Mistral high-efficiency nebulisation system has previously been described.¹⁵

Seven Faraday detectors were utilised in this study. These were referenced from the low to the high side of the electromagnet as low 2; low 1; axial; high 1; high 2; high 3 and high 4. The relative position of these detectors was adjusted so as to allow a simultaneous measurement

of ^{202}Hg in low 2, ^{203}Tl in low 1, ^{204}Pb in axial, ^{205}Tl in high 1, ^{206}Pb in high 2, ^{207}Pb in high 3 and ^{208}Pb in high 4. A comparison of the measured $^{205}\text{Tl}/^{203}\text{Tl}$ ratio with the accepted value of 2.3871¹⁶ allowed a calculation of the mass bias. This mass-bias figure was then applied to simultaneously correct the measured lead ratios. A measurement and correction for mass bias was made using the following simple power relationship:

$$R_{\text{true}} = R_{\text{meas}} (1 + C)^{\delta m}, \quad (1)$$

where R_{true} is the true value, R_{meas} the measured value, C the mass bias factor and δm the mass difference. A high-precision measurement of the hafnium and neodymium reference materials has revealed a power-law equation¹⁰ to be a more accurate correction for the mass bias than a simpler linear-law equation.

A magnet scan between masses 195 and 205 amu revealed the presence of mercury both within the sample solutions and as a background contaminant. Since mercury has a great affinity for glassware, it exhibits a relatively long memory effect. The mercury ion signal was equivalent to a solution of approximately 30 ppt mercury. Thus, the ^{204}Hg isotope contributed approximately 0.5% to the intensity of the ^{204}Pb signal. If this was not corrected it would result in a falsely high ^{204}Pb measurement. Therefore, the ^{202}Hg isotope was also measured and the magnitude of ^{204}Hg was calculated assuming an $^{204}\text{Hg}/^{202}\text{Hg}$ isotope ratio of 0.2293.¹⁷ The true ^{204}Pb intensity was determined by subtraction.

Prior to analysis, the amplification circuitry associated with each Faraday detector was calibrated with a 10 V calibration signal and referenced to the axial amplifier.

Each solution of NIST SRM Pb981, pond sediment, airborne particulates and Merck multielement standard was divided into six samples for analysis. Each sample was analysed for 50 s, *i.e.* 10 measurements each of 5 s duration. The following isotope ratios were measured: $^{202}\text{Hg}/^{204}\text{PbHg}$; $^{205}\text{Tl}/^{203}\text{Tl}$; $^{208}\text{Pb}/^{204}\text{Pb}$; $^{207}\text{Pb}/^{204}\text{Pb}$; $^{206}\text{Pb}/^{204}\text{Pb}$; $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$. Because thallium was used to simultaneously correct for the mass bias the analysis of a normalisation sample was not necessary. However, the NIST SRM Pb981 solution

was analysed first in order to assist in quantifying the accuracy of the experimental techniques.

Results and Discussion

The lead isotope ratios measured for 6 samples of the 50 ng ml⁻¹ NIST SRM Pb981 are shown in Table 1. Each figure represents the measurement of 1 sample, and is the mean value of 10 measurements, each of 5 s duration. The values in parenthesis represent the %standard error (%SE) associated with each sample measurement. The sample uptake was approximately 0.4 ml min⁻¹, and each analysis procedure took 100 s; thus, the analysis of each sample used about 35 ng of lead. The calculation of the sample usage assumed a sample analysis time equal to twice the acquisition period, thus allowing for signal stabilisation, periodic base-line measurement and data manipulation. Six samples of the reference material were measured; the grand mean for each ratio is given at the foot of Table 1. The total analysis time for the measurement of six samples was about 15 min, which is comparable to that taken by the quadrupole study.⁸ The analysis of the 50 ng ml⁻¹ Pb981 reference material with the Mistral desolvation system resulted in a total lead ion current of approximately 2×10^{-11} A. This is equivalent to a total of 2.5×10^9 lead ions detected per second for a 1 $\mu\text{g ml}^{-1}$ solution. This is 10–100 times greater than that observed with a quadrupole instrument operated under similar conditions (an electromagnet, unlike a quadrupole, transmits 100% of the intended element). Desolvation of the aerosol resulted in a factor of 7 increase in the ion signal levels, compared to conventional nebulisation.¹⁰

The measurements of the Pb981 isotope ratios, $^{208}\text{Pb}/^{204}\text{Pb}$; $^{207}\text{Pb}/^{204}\text{Pb}$; $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$, agree with the certified values determined by TIMS. The levels of precision quoted in this study are superior to those quoted by NIST. This is probably because a thermal source mass spectrometer exhibits a time-dependent sample fractionation that is difficult to either control or predict. In contrast, the Plasma 54 exhibits a

Table 1 Analysis of NIST Pb981, 50 ppb

Sample	208/204	207/204	206/204	208/206	206/207
#1	36.684 (0.023)	15.491 (0.020)	16.931 (0.020)	2.1667 (0.006)	1.09306 (0.005)
#2	36.696 (0.011)	15.495 (0.014)	16.942 (0.013)	2.1661 (0.007)	1.09328 (0.003)
#3	36.696 (0.010)	15.494 (0.009)	16.939 (0.010)	2.1662 (0.003)	1.09335 (0.003)
#4	36.711 (0.015)	15.501 (0.013)	16.946 (0.013)	2.1663 (0.006)	1.09324 (0.003)
#5	36.683 (0.010)	15.491 (0.010)	16.938 (0.009)	2.1658 (0.005)	1.09339 (0.005)
#6	36.687 (0.011)	15.490 (0.010)	16.938 (0.009)	2.1659 (0.005)	1.09346 (0.002)
Mean	36.693	15.494	16.939	2.1662	1.09330
2SD	0.021	0.008	0.010	0.0006	0.0003
%RSD	0.029	0.026	0.029	0.015	0.013
NIST	36.721	15.491	16.937	2.1681	1.09337

Values in parenthesis are the SE (%).

time-independent mass bias that can be corrected with a measurement of the thallium isotope ratio. The measured value of $^{208}\text{Pb}/^{206}\text{Pb}$ differs significantly from the value certified by NIST; this has also been noted by other workers and has previously been discussed.¹⁰

Tables 2, 3 and 4 detail the Plasma 54 analysis of 6 samples of pond sediment, airborne particulates and the Merck multielement standard, respectively. Signal levels were proportionately equivalent to that obtained with the SRM Pb981 solution. Each figure represents the measurement of 1 sample and is the mean value of 10 measurements each of 5 s duration. The values in parenthesis represent the %SE associated with each sample measurement. The analysis of each aliquot of

pond sediment utilised 55 ng of lead, the Airborne Particulates 30 ng and the Merck multielement standard 70 ng. The levels of analytical precision are comparable to those obtained from the measurement of the Pb981 reference material. Each materials has a characteristic set of measured isotope ratios, each ratio being significantly different for each sample. This is in contrast to the measurements obtained by quadrupole mass spectrometry, in which the isotope ratios measured for some samples cannot be significantly differentiated. Thus, the Plasma 54 mass spectrometer demonstrates the ability to determine very small differences in isotopic composition, thereby increasing the range of possible applications.

Table 2 Analysis of NIES Pond Sediment, 80 ppb

Sample	208/204	207/204	206/204	208/206	206/207
#1	37.672 (0.024)	15.548 (0.034)	17.757 (0.027)	2.1215 (0.009)	1.14244 (0.004)
#2	37.676 (0.020)	15.547 (0.018)	17.765 (0.025)	2.1213 (0.010)	1.14243 (0.010)
#3	37.685 (0.029)	15.546 (0.017)	17.755 (0.020)	2.1220 (0.016)	1.14201 (0.005)
#4	37.680 (0.027)	15.549 (0.026)	17.758 (0.026)	2.1219 (0.008)	1.14207 (0.008)
#5	37.704 (0.022)	15.559 (0.023)	17.774 (0.025)	2.1212 (0.004)	1.14239 (0.006)
#6	37.652 (0.048)	15.536 (0.049)	17.760 (0.053)	2.1202 (0.009)	1.14326 (0.007)
Mean	37.678	15.547	17.762	2.1214	1.14243
2SD	0.034	0.015	0.014	0.0013	0.00089
%RSD	0.045	0.047	0.039	0.031	0.039

Values in parenthesis are the SE (%).

Table 3 Analysis of NIES Airborne Particulates, 45 ppb

Sample	208/204	207/204	206/204	208/206	206/207
#1	37.911 (0.020)	15.587 (0.017)	17.967 (0.014)	2.1099 (0.005)	1.15272 (0.005)
#2	37.913 (0.018)	15.590 (0.012)	17.969 (0.010)	2.1099 (0.004)	1.15263 (0.005)
#3	37.917 (0.018)	15.588 (0.016)	17.969 (0.019)	2.1102 (0.008)	1.15271 (0.008)
#4	37.904 (0.017)	15.583 (0.016)	17.968 (0.017)	2.1094 (0.004)	1.15306 (0.005)
#5	37.934 (0.029)	15.594 (0.031)	17.975 (0.027)	2.1104 (0.011)	1.15276 (0.005)
#6	37.908 (0.025)	15.586 (0.026)	17.968 (0.025)	2.1097 (0.005)	1.15286 (0.004)
Mean	37.915	15.588	17.969	2.1099	1.15279
2SD	0.021	0.007	0.006	0.0007	0.0003
%RSD	0.028	0.024	0.016	0.017	0.013

Values in parenthesis are the SE (%).

Table 4 Analysis of Merck Standard, 100 ppb

Sample	208/204	207/204	206/204	208/206	206/207
#1	38.473 (0.016)	15.733 (0.016)	19.250 (0.015)	1.9985 (0.006)	1.22353 (0.006)
#2	38.461 (0.017)	15.728 (0.017)	19.245 (0.018)	1.9984 (0.005)	1.22362 (0.003)
#3	38.474 (0.008)	15.733 (0.008)	19.253 (0.008)	1.9982 (0.004)	1.22375 (0.004)
#4	38.472 (0.013)	15.733 (0.012)	19.256 (0.010)	1.9979 (0.008)	1.22395 (0.006)
#5	38.487 (0.014)	15.741 (0.009)	19.266 (0.012)	1.9976 (0.002)	1.22400 (0.004)
#6	38.489 (0.022)	15.738 (0.020)	19.261 (0.017)	1.9983 (0.006)	1.22384 (0.005)
Mean	38.476	15.734	19.255	1.9982	1.22378
2SD	0.021	0.009	0.015	0.0007	0.00037
%RSD	0.027	0.029	0.039	0.017	0.015

Values in parenthesis are the SE (%).

The Merck multielement solution contains 23 elements (Ag; Al; B; Ba; Bi; Ca; Cd; Co; Cr; Cu; Fe; Ga; In; K; Li; Mg; Mn; Na; Ni; Pb; Sr; Tl and Zn) each at a concentration of 100 ng ml⁻¹. The pond sediment and airborne particulate samples were analysed for trace elements by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).⁸ The analytical results for each sample are given in Table 5; both contain a considerable concentration of Al and Fe. The ability of a plasma source mass spectrometer to determine the isotope ratios of elements within such contaminated solutions is of considerable analytical importance and it offers a major advantage over TIMS.

A comparison of the ratios determined by the inter

laboratory groups, including the measurements obtained with the Plasma 54 mass spectrometer, are given in Table 6. The column headings refer to the participants and type of instrument used; these are detailed in Table 7. Yokogawa Electric Co. measured each isotope for a time period in inverse proportion to its natural abundance (Yokogawa 2) and measured each isotope for an equal period of time (Yokogawa 1). The measurement errors in Table 6 are expressed as 2 standard deviations (2SD). The errors presented by Furuta in reference number 8 refer to a measurement of the normalisation sample; these errors have been doubled in order to include the measurement and correction of the sample solutions. The Plasma 54 demonstrates a factor of 10–100 improvement in precision compared to the quadrupole investigations. Although the errors associated with each quadrupole instrument are relatively high, the majority of the ²⁰⁶Pb/²⁰⁷Pb measurements agree with those determined with the Plasma 54. However, the measurement of the ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb isotope ratios show considerable variation between studies. This is due to the relatively low abundance of the ²⁰⁴Pb isotope, which increases the level of analytical error.

While a comparison of precision levels can easily be quantified, an assessment of the relative accuracy is more difficult. A high-precision analysis utilising an alternative instrumental technique is ideally required. However, there are several reasons why the authors believe that an analysis with the Plasma 54 system is more accurate than that using the quadrupole systems. The Plasma 54 analysis of SRM Pb981 in this study and the analysis of SRMs Pb981 and Pb983 in a previous study¹⁰

Table 5 ICP-AES Elemental Analysis of Pond Sediment and Airborne Particulates (ng/g)

Element	λ /nm	Pond Sediment	Airborne Particulates
Al	308.22	102000	46200
Fe	259.94	68000	46600
Ti	334.90	5690	3420
Ca	393.37	8340	57500
Mg	279.55	8270	10700
Na	589.00	6080	14400
P	214.91	1250	2350
Mn	257.61	640	870
Zn	213.86	350	2400
V	292.40	240	120
Cu	324.75	190	610
Pb	220.35	81	447
Cr	267.72	56	160

Table 6 Interlaboratory comparison of lead isotope ratios determined by ICP-MS

	Plasma 54	NIES	Plymouth	NRC	NCL	Yokogawa 1	Yokogawa 2	Turner	Indiana
Pond Sediment									
206/204	17.762	17.767	17.881	17.793	18.114	17.797	17.729	18.48	20.590
2SD	0.014	0.428	2.068	0.196	0.340	0.440	0.240	0.92	1.34
206/207	1.1424	1.1426	1.1444	1.1475	1.1435	1.1426	1.1426	1.159	1.1516
2SD	0.0009	0.0132	0.0252	0.0196	0.0092	0.0100	0.0212	0.008	0.0464
208/204	37.678	37.476	37.706	37.539	38.836	37.889	37.870	38.71	41.736
2SD	0.034	0.812	4.328	1.204	0.964	0.904	0.728	1.96	2.74
Airborne Particulates									
206/204	17.969	18.148	18.198	18.292	17.980	17.946	17.914	18.26	18.081
2SD	0.006	0.428	2.068	0.196	0.340	0.440	0.240	0.92	1.34
206/207	1.1528	1.1567	1.1574	1.1585	1.1493	1.1528	1.1524	1.160	1.1124
2SD	0.0003	0.0132	0.0252	0.0196	0.0092	0.0100	0.0212	0.008	0.0464
208/204	37.915	38.516	38.187	39.046	37.648	37.897	37.788	37.97	36.358
2SD	0.021	0.812	4.328	1.204	0.964	0.904	0.728	1.96	2.74
Merck Multielement Standard									
206/204	19.255	18.906	19.741	18.084	18.446	18.836	18.884	17.42	17.231
2SD	0.015	0.428	2.068	0.196	0.340	0.440	0.240	0.92	1.34
206/207	1.2238	1.2253	1.2198	1.2272	1.2209	1.2226	1.2271	1.172	1.2924
2SD	0.0004	0.0132	0.0252	0.0196	0.0092	0.0100	0.0212	0.008	0.0464
208/204	38.476	38.226	39.464	36.114	37.177	37.702	37.803	36.40	33.366
2SD	0.021	0.812	4.328	1.204	0.964	0.904	0.728	1.96	2.74

Table 7 Participants and instruments used in the inter-laboratory comparison study (Ref. 8)

Participant	Instrument
Dr. Joseph Lam and Dr. James W. McLaren (National Research Council of Canada)	Sciex ELAN 250
Dr. Simon Sparkes (Plymouth Polytechnic)	VG PlasmaQuad II
Ms. Naoko Shibata and Dr. Masaaki Kubota (National Chemical Laboratory for Industry)	Seiko SPQ 6100
Ms. Yoko Kishi and Dr. Ken-ichi Sakata (Yokogawa Electric Corporation)	Yokogawa PMS 2000
Dr. P. Turner (Turner Scientific) and C. W. McLeod (Sheffield City Polytechnic)	Turner TS SOLA
Dr. David P. Myers and Gary M. Hieftje (Indiana University)	Lab constructed Balzers mass spectrometer
Dr. Naoki Furuta (National Institute for Environmental Studies)	VG PlasmaQuad II

agree with the certified values. This agreement is due in part to the use of thallium as a correction for the mass bias, and a simultaneous measurement of the isotopic components. In addition, the Plasma 54 exhibits "flat top" peak shapes that allow an accurate quantification of each isotopic component. This study also corrected for the ^{204}Hg interference with ^{204}Pb by simultaneously measuring the ^{202}Hg isotope.

References

1. T. J. Chow, C. B. Snyder and J. L. Earl, *Isot. Ratios Pollut. Source Behav. Indic., Proc. Symp., IAEA, 1974* (Pub. 1975), pp. 95 – 108.
2. S. Facchetti, F. Geiss, P. Gaglione, A. Colombo, G. Garibaldi, G. Spallanzani and G. Gille, "Isotopic Lead Experiment-Status Report", EUR 8352 EN, pp. 1 – 112, Commission of the European Communities, Brussels, 1984.
3. G. Faure, "*Principles of Isotope Geology*", Wiley, New York, 1986.
4. W. T. Sturges and L. A. Barrie, *Nature* [London], **329**, 144 (1987).
5. H. T. Delves and M. J. Campbell, *J. Anal. At. Spectrom.*, **3**, 343 (1988).
6. M. J. Campbell and H. T. Delves, *J. Anal. At. Spectrom.*, **4**, 235 (1989).
7. K. E. Jarvis, A. L. Gray and R. S. Houk, "*Handbook of Inductively Coupled Plasma Mass Spectrometry*", Blackie, Glasgow and London, 1992.
8. N. Furuta, *Anal. Sci.*, **7**, 823 (1991).
9. A. J. Walder and P. A. Freedman, *J. Anal. At. Spectrom.*, **7**, 571 (1992).
10. A. J. Walder, I. Platzner and P. A. Freedman, *J. Anal. At. Spectrom.*, **8**, 19 (1993).
11. H. P. Longerich, B. J. Fryer and D. F. Strong, *Spectrochim. Acta*, **42B**, 39 (1987).
12. M. E. Ketterer, M. J. Peters and P. J. Tisdale, *J. Anal. At. Spectrom.*, **6**, 439 (1991).
13. P. Sigsworth, J. Stringer and R. C. Hutton, Poster presented at the 1992 Conference on Plasma Source Mass Spectrometry, Durham, September 13th – 18th, 1992.
14. A. R. Eastgate, R. C. Fry and G. H. Gower, *J. Anal. At. Spectrom.*, **8**, 305 (1993).
15. A. J. Walder, D. Koller, N. M. Reed, R. C. Hutton and P. A. Freedman, *J. Anal. At. Spectrom.*, **8**, 1037 (1993).
16. L. P. Dunstan, J. W. Gramlich, I. L. Barnes and W. C. Purdy, *J. Res. Natl. Bur. Stand.*, **85**, 1 (1980).
17. P. DeBièvre, M. Gallet, N. E. Holden and I. L. Barnes, *J. Phys. Chem. Ref. Data*, **13**, 877 (1984).

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